Gold Catalysis

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The [4+2], not [2+2], Mechanism Occurs in the Gold-Catalyzed Intramolecular Oxygen Transfer Reaction of 2-Alkynyl-1,5-Diketones**

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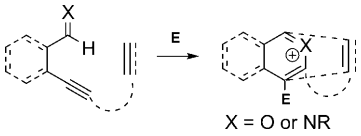
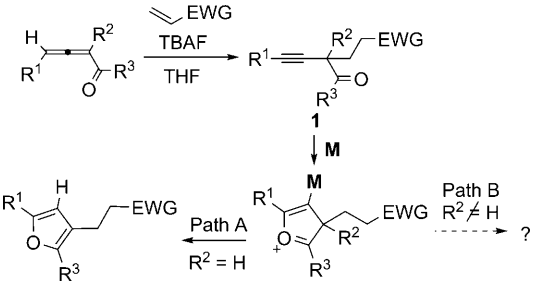
The chemistry of the oxonium and aminium ions formed from alkynylic aldehydes or imines by transition metals, Lewis acids, Brønsted acids, or even electrophiles such as iodine (Scheme 1), has attracted wide interest. These intermediates undergo both intermolecular and intramolecular cycloadditions to carbon–carbon multiple bonds, to give myriad products of synthetic importance.[1,2–10]

Recently, we developed a convenient approach to 2-alkynyl-1,5-dicarbonyl derivatives, **1**, from the Michael addition of activated allenes to electron-deficient olefins.[11] We envisioned that if a furanium intermediate[12] (Scheme 2) could be generated from the alkynylketone **1** containing a quaternary propargylic carbon, then the usual path A[12] would be blocked, leaving path B to engender novel transformations of the oxonium intermediate.

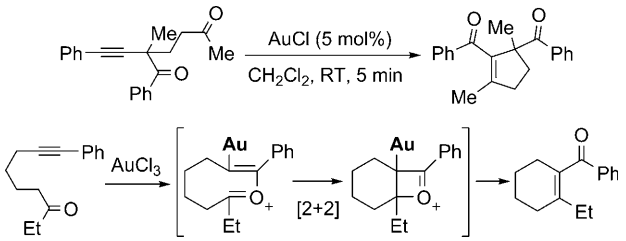
We have now found that after only 5 min at room temperature, using gold catalysis,[13,14] 2-alkynyl-1,5-diketone **1a** furnished cyclopentenylketone **2a**—an intramolecular oxygen transferred product—in excellent yield (Scheme 3, top).



Scheme 1. Formation of oxonium or aminium ions from alkynylic aldehydes or imines.



Scheme 2. Formation of furanium ions from propargylic ketones.



Scheme 3. Gold-catalyzed intramolecular oxygen transfer of alkynylketones.

Of special interest is the oxygen transfer from a carbonyl group to a carbon–carbon triple bond through an oxonium intermediate, also known as alkyne–carbonyl metathesis.[15] This has also been showcased in Yamamoto and co-workers' recent papers on gold or TfOH-catalyzed intramolecular oxygen transfer of ω-alkynylketones to the corresponding cyclic enones (Scheme 3, bottom).[16] A [2+2] pathway has been invoked for this oxygen transfer.[15,16]

A [2+2] pathway might be invoked to rationalize the outcome in our gold-catalyzed, intramolecular oxygen transfer of 2-alkynyl-1,5-diketones to form the corresponding cyclopentenylketones. However, the fact that this reaction could be completed in minutes at room temperature, and with higher yields than those of previously reported oxygen transfers,[15,16] prompted us to propose an alternative [4+2] mechanism (Scheme 4), and to investigate the scope of this reaction. Herein, we describe the results from experimental and theoretical investigations that establish this new mechanism.

To elucidate which pathway—the well-accepted [2+2] mechanism or our newly proposed [4+2] pathway[17]—was responsible for the gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,5-diketones, we designed an isotopic

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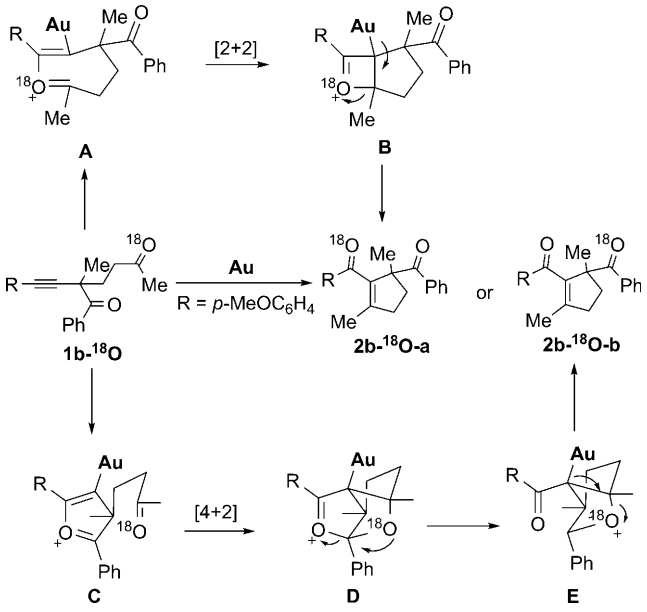


Scheme 4. Isotopic labeling experiment for mechanistic studies.

labeling experiment (Scheme 4). We speculated that if an ^{18}O atom could be incorporated into one of the carbonyl groups of the substrate, then the ^{13}C NMR spectrum[18] of the reaction product could be used to locate the ^{18}O atom, and provide clues as to the more favorable mechanistic pathway. Hence, using alkynyldiketone **1b-^{18}O** (R = *p*-methoxyphenyl) as a model substrate, if the reaction follows a [2+2] route then ^{18}O would end up on the left carbonyl group in **2b-^{18}O-a** (Scheme 4, top), whereas it would be incorporated on the benzoyl group in **2b-^{18}O-b** if the reaction follows a [4+2] pathway (Scheme 4, bottom).

Substrate **1b-^{18}O** was synthesized from the ^{18}O exchange of compound **1b** with $H_2{}^{18}O$ under acidic condition (Figure 1).[19] The ^{18}O exchange happened only at the methyl carbonyl group, as indicated by ^{13}C NMR spectroscopy. A $\delta = 0.05$ ppm (5 Hz) upfield chemical shift[18] was found on carbon 1, whereas no chemical shift change occurred on carbon 2. With substrate **1b-^{18}O** in hand, we carried out the gold-catalyzed oxygen transfer reaction and the product **2b-^{18}O** was obtained in quantitative yield (Figure 2), without any ^{18}O loss as determined by its ESI mass spectrum. It was found that only carbon 4 in the product **2b-^{18}O** exhibited the $\delta = 0.05$ ppm (5 Hz) upfield chemical shift in its ^{13}C NMR spectrum (also see Supporting Information). The absence of any detectable ^{18}O incorporation at carbon 3 demonstrates that the [2+2] pathway is disfavored, and instead it is a [4+2] pathway that is the favored mechanism for the gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,5-diketones.

Since our experimental studies established the [4+2] pathway to be the preferred mechanism, we turned to quantum chemical calculations to seek further verification of the preferred pathway and to understand the origins of the selectivity.[20] We performed calculations at the "double-hybrid" density functional level of theory with the B2PLYP functional. This method replaces a fraction of the semi-local correlation energy by a non-local correlation energy expression that employs the Kohn–Sham orbitals in second-order perturbation theory and delivers improved energetics over hybrid density functionals such as B3LYP. Results obtained at this level were also compared with the standard B3LYP and M06-2X functionals, and from single-point energy calculations at the SCS-MP2 level: we found that all methods were in agreement over the preferred mechanism (for a full comparison refer to the Supporting Information). DFT studies of Au^I catalysis have been shown to give qualitative and quantitative insight into the catalytic cycle.[21] All calculations were performed with Gaussian 09[22] and use a LANL2DZ effective core potential for Au and Pople double or triple-ζ basis sets for all other elements.[23]

The competing [2+2] and [4+2] reaction coordinates were computed for the substrate shown in Scheme 5. Calculations were also performed for a larger substrate for which the aryl groups of **1a** are modeled by phenyl groups, giving very similar results. The computed reaction coordinate for each substrate is shown in full in the Supporting Information. In accord with our experimental findings, the [4+2] pathway is

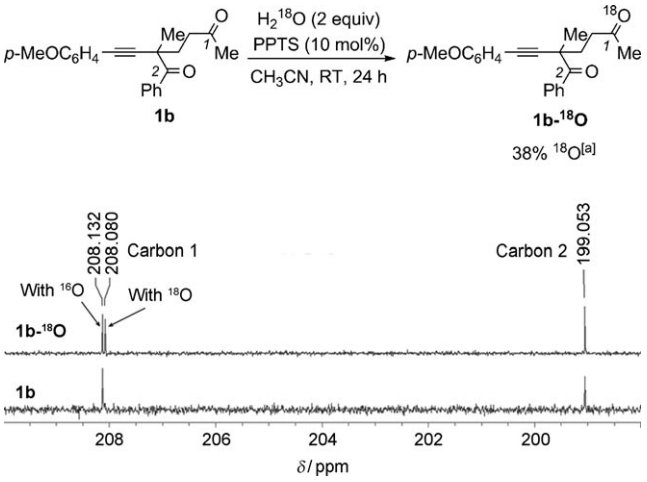


Figure 1. Synthesis of substrate **1b-^{18}O** and the ^{13}C NMR spectrum. [a] Determined by MS (ESI).

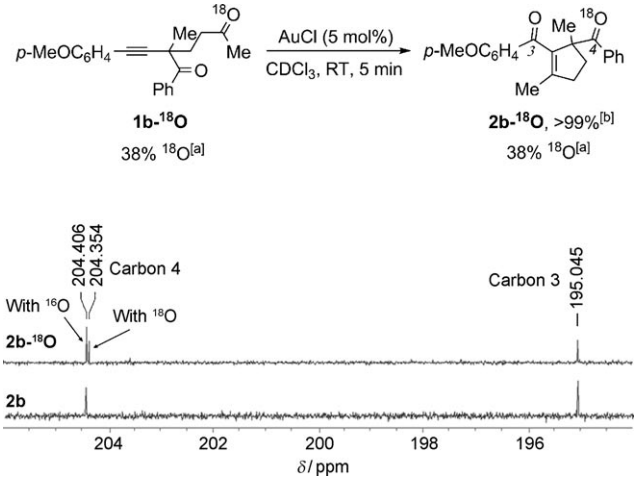
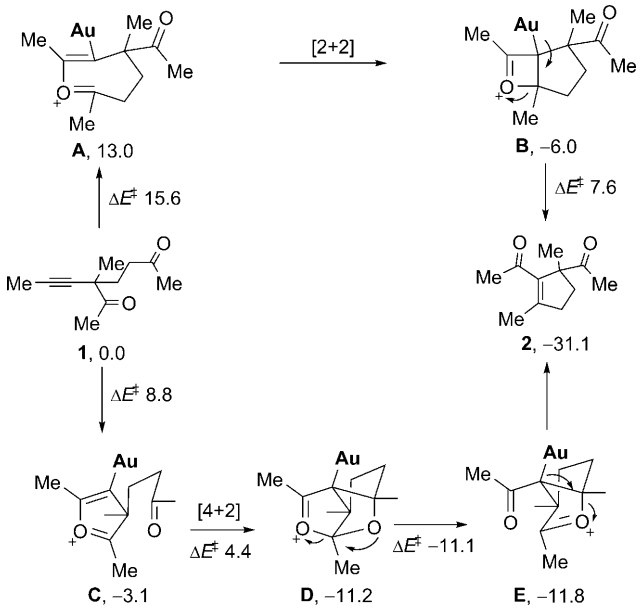


Figure 2. ^{18}O isotopic experiment and the ^{13}C NMR spectrum. [a] Determined by MS (ESI). [b] NMR yield.



Scheme 5. B2PLYP/6-311+G(d,p)//B2PLYP/6-31G(d) computed reaction profile. Relative energies in kcal mol^{-1}.

computed to be the more favorable. The rate-limiting step in each pathway is the intramolecular nucleophilic addition to the Au-coordinated alkyne—the barrier for this step is computed to be 6.8 kcal mol^{-1} lower for the formation of the five-membered ring oxonium intermediate **C** than for seven-membered ring oxonium **A**. This energetic preference is also observed in the stabilities of the oxonium ions themselves, with **C** considerably more stable by 16.1 kcal mol^{-1}. The subsequent transformations are all computed to be feasible, with the barrier to [4+2] cyclization lying only 4.4 kcal mol^{-1} above the starting complex.

The key transition structures for the intramolecular alkyne addition are shown in Figure 3, along with the [4+2] cyclization transition state (TS). Why is 5-*endo*-dig **TS-4** so drastically preferred over 7-*endo*-dig **TS-1**? By way of comparison, we computed the barrier for the intermolecular addition of acetone to Au-coordinated butyne to be 19.3 kcal mol^{-1}, so **TS-4** appears to be remarkably stable rather than any inherent instability of **TS-1**. Acceleration of the ring-closing due to the presence of a quaternary center cannot fully explain the low barrier of 8.8 kcal mol^{-1}, since replacing this carbon with methylene only raises the barrier by 0.7 kcal mol^{-1}. However, **TS-4** does benefit from an almost planar

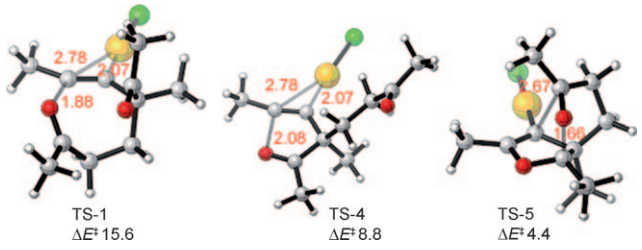
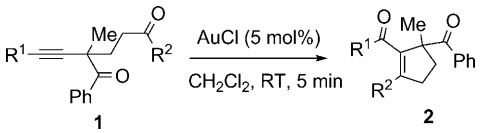


Figure 3. B2PLYP/6-31G(d) transition structures for addition to the alkyne and for [4+2] cyclization.

dihedral angle (0.8°) between the alkyne and attacking carbonyl not present in TS-1 due to the constraints of the 7-membered ring (48.9°), and also in the intermolecular reaction (75.8°) due to sterics. The low computed barrier for **TS-4** is consistent with the rapid conversion seen experimentally. **TS-5** is concerted but highly asynchronous, with forming bond lengths of 1.66 Å (C–O) and 2.67 Å (C–C), and lies only 4.4 kcal mol^{-1} above the starting complex. Overall, the large energetic preference of **TS-4** over **TS-1**, which was seen at all levels of theory we tested, supports the idea that the [4+2] pathway is dominant in the gold-catalyzed oxygen transfer of 2-alkynyl-1,5-diketones, which is in accordance with our ^{18}O isotopic experiments.

We then proceeded to investigate the scope of this gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,5-diketones. Both aromatic and aliphatic-containing substrates were screened, and the corresponding products **2b**–**2j** were obtained in excellent yields (Table 1).

Table 1: Gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,3-diketones.[a]



Entry	R^1, R^2	Yield [%]/**2**[b]
1	C_6H_5, Me **1a**	**2a**, 98
2	*p*-$MeOC_6H_4$, Me **1b**	**2b**, 99
3	*p*-ClC_6H_4, Me **1c**	**2c**, 92
4	*n*-C_6H_{13}, Me **1d**	**2d**, 99
5	*i*Pr, Me **1e**	**2e**, 96
6	*t*Bu, Me **1f**	**2f**, 95
7	Me, Me **1g**	**2g**, 91
8	Bn, Me **1h**	**2h**, 94
9	CypCH2, Me **1i**	**2i**, 99
10	Ph, Et **1j**	**2j**, 98

[a] General reaction conditions: 2-alkynyl-1,5-diketone **1** 0.3 mmol, CH_2Cl_2 2.0 mL. [b] Yields of isolated product.

In conclusion, we have discovered a novel [4+2] pathway for the gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,5-diketones to cyclopentenylketones. This mechanism was confirmed by ^{18}O isotopic labeling experiments and quantum chemical calculations. Various substrates were employed in the reaction and the corresponding products were obtained in excellent yields under very mild conditions. Further exploration and applications of this methodology and calculations on the mechanism are underway in our groups.

Experimental Section

General procedure for gold-catalyzed oxygen transfer of 2-alkynyl-1,5-diketones to the corresponding cyclopentenylketones: To a solution of 2-methyl-1-phenyl-2-(phenylethynyl)hexane-1,5-dione (**1a**; 46 mg, 0.20 mmol) in dichloromethane (1.0 mL) was added AuCl (2 mg, 0.010 mmol). The mixture was stirred for 5 min at room temperature. Afterwards the solvent was removed under reduced pressure and the residue was subjected to a flash column chromatography (eluent: ethyl acetate/*n*-hexane 1:15) to give product **2a** (45 mg,

98%) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2968, 2930, 1673, 1645, 1596, 1446, 1283, 973 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.58 (3H, s), 1.70 (3H, s), 2.14–2.18 (1H, m), 2.48–2.53 (1H, m), 2.56–2.61 (1H, m), 2.76–2.78 (1H, m), 7.39–7.55 (6H, m), 7.48–7.84 ppm (4H, t, J = 7.0 Hz)); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 17.2, 24.5, 36.0, 38.5, 65.5, 128.1, 128.4, 128.5, 129.3, 131.4, 132.4, 137.3, 139.4, 140.8, 148.7, 196.5, 204.5 ppm. Anal. calcd. for $C_{21}H_{20}O_2$: C 82.86, H 6.62; found: C 82.68, H 6.76.

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